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ACCURATE AB INITIO CALCULATIONS FOR THE $^1B_1 - {}^1A_1$

SEPARATION IN METHYLENE

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Accurate ab initio Calculations for the ${}^1B_1 - {}^1A_1$ Separation in Methylene

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Abstract

Accurate ab initio calculations have been performed on the ${}^1B_1$ State of methylene. The basis set was of better than triple-zeta quality and included two sets of polarization functions. This work combined with previous work yields a ${}^1A_1 - {}^1B_1$ separation of 1.07 eV. This determination of the ${}^1A_1 - {}^1B_1$ separation is compared to those using Franck-Condon factors.

Harding and Goddard[1] (HGI) computed accurate ab initio potential energy surfaces for the three lowest states of CH_2. Because of the intrinsic limitations of their calculations, they were unable to definitively determine the separations between the various states of methylene. In order to resolve this uncertainty Harding and Goddard[2] (HGII) then computed the Franck–Condon factors from their calculated curves. HGII found it necessary to make several approximations in order to bring the computed and experimental spectra into coincidence. They shifted the $^2B_1$ curve of CH_2^- down by 0.02926 h to match the experimental $^1A_1 - ^2B_1$ 0–0 transition, they shifted the $^3B_1$ curve up by 0.06 eV, and they corrected the $^2B_1$ vibrational spacings based on the computed error for the $^1A_1$ bending frequency. They made no such correction for the $^3B_1$ vibrational spacing, this was based on the fact that the computed $^1B_1$ vibrational spacings were in excellent agreement with experiment, however, unlike the $^2B_1$ and $^1A_1$ curves where the well depth was the same, the $^3B_1$ and $^1B_1$ curves have well depths that differ by a factor of two.

Shih, Peyerimhoff, Buenker, and Peric[3] (SPBP) also computed ab initio potential curves and the associated Franck–Condon factors. SPBP were able to bring the computed Franck–Condon factors into reasonable agreement with experiment by shifting the $^2B_1$ curve by −0.24 eV and the $^3B_1$ curve by 0.01 eV.

Based on their calculations SPBP concluded the $^1A_1$-$^1B_1$ separation

was 11.5 kcal/mole, while HGII computed a separation of 9.0±1.0

kcal/mole. The HGII result is in agreement with our[4] previous estimate

of 9 kcal/mole, the recent work of Lengel and Zare[5] and the large

number of chemical determinations[6-10] in the range of 7-8 kcal/mole.

All three results[2-4] differ from the 19.4 kcal/mole of Zittel et al.[11].

In general high spin states are computed more accurately than the

low spin states. The accurate atomic calculations of Sasaki and

Yoshimine[12] indicate that this error is about 2 kcal/mole for carbon.

We noted this fact and shifted the $^1A_1$ state of CH_2 down, relative to

the $^3B_1$ state by 2 kcal/mole. HGII found it necessary to shift the

$^1A_1$ curve down by 0.06 eV (1.4 kcal/mole), which agrees with our

results in both size and direction. SPBP, however shifted the $^1A_1$

state up by 0.01 eV, which would appear to be the wrong direction. The

surprising fact is that SPBP found agreement between the computed

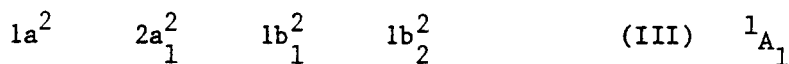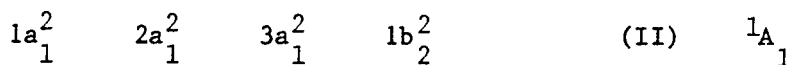Franck-Condon factors and experiment with this shift.

HGII computed the $^1B_1$-$^1A_1$ separation and assigned the last

observed transition as v=5 to v=0, yielding a 0-0 transition of 1.08±

0.05 eV. SPBP made a similar assignment, and computed the T_0 to be

1.10 eV. This assignment is different form that of Herzberg and

Johns[13], who assigned the last observed transition as 6-0.

In light of the numerous approximations HGII were forced to make

in order to bring the computed Franck-Condon factors in agreement with

experiment, the fact that HGII's ratio of intensity to $^1A_1$ and to $^3B_1$

is 0.44 rather than the observed 0.76, and the fact that SPBP and HGII were able to compute different $^1A_1-^3B_1$ separations while using the same technique, it would seem valuable to determine the $^1A_1-^1B_1$ separation by a different method. As before, we estimate the size and direction of the remaining error based on trends observed for CH_2 with differing basis sets and trends observed for the separation in the corresponding states of CH.

The basis sets used are the same as in the previous study of methylene.[4] The double zeta (DZ) set is Dunning's contraction[14] of the Huzinaga[15] 9s5p primitive set for carbon and the 4s set for hydrogen (scaled by 1.2). The double zeta plus polarization (DZP) basis set starts with the DZ set and adds a set of d functions ($\alpha=0.75$) to the carbon and a set of p functions ($\alpha=1.0$) to the hydrogens. The large basis set is a better than triple zeta contraction of the primitive sets of van Duijneveldt[16] with two sets of polarization functions added; C(12s7p2d/6s4p2d) and H(6s2p/3s2p). The exponents of the polarization functions are those recommended by van Duijneveldt;[16] 1.4 and 0.25 (p) and 1.5 and 0.35 (d).

The carbon inner-shell orbital ($1a_1$) is held doubly occupied in all configurations in the present CI calculations. Otherwise, all single and double excitations for one principle configuration are included for the $^1B_1$ and $^3B_1$ states while all single and double excitations from two reference configurations are included for the $^1A_1$ state. The reference configurations are:

$$1a_1^2 \qquad 2a_1^2 \qquad 3a_1^1 \qquad 1b_1^1 \qquad 1b_2^2 \qquad (I) \qquad {}^{1,3}B_1$$

$$1a_1^2 \qquad 2a_1^2 \qquad 3a_1^2 \qquad 1b_2^2 \qquad\qquad (II) \qquad {}^{1}A_1$$

$$1a^2 \qquad 2a_1^2 \qquad 1b_1^2 \qquad 1b_2^2 \qquad\qquad (III) \qquad {}^{1}A_1$$
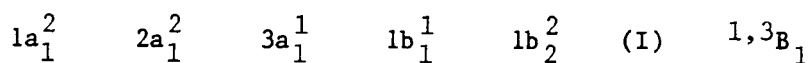
For the ${}^{1}B_1$ and ${}^{3}B_1$ states we used orbitals obtained from a single configuration SCF calculation, while for the ${}^{1}A_1$ state was used orbitals obtained from a two configuration (II and III) MCSCF calculation. The differential effect of the quadruple excitations on the ${}^{1}B_1 - {}^{3}B_1$ separation is accounted for using Davidson's formula.[17] For the large basis set, this was found to reduce the separation by only 0.01 eV. For the ${}^{1}A_1$ state the two reference calculations were used, and as we showed previously,[4] this satisfactorily accounts for the differential quadruple effects. The ${}^{1}A_1$ one reference with the Davidson correction gives essentially the same results as the 2 reference ${}^{1}A_1$, reducing the ${}^{1}A_1 - {}^{1}B_1$ separation by only 0.01 eV. (A more complete description of the ${}^{1}A_1$ and ${}^{3}B_1$ calculations can be found in reference 4.) All CI calculations were performed using the programs developed and implemented by Shavitt and coworkers.[18]

The geometry was optimized at the CI level using the DZP basis for the $^1B_1$ state. The computed values are in very good agreement with experiment;[13] R(CH)=1.077Å (1.05Å) and <=141.5° (140°). The large basis calculations were run at this optimized geometry. The results are summarized in Table I and Table II.

Previously[4] we observed that the energy of the $^1A_1$ state decreased relative to the $^3B_1$ state as the basis set was improved. This work indicates that the $^1B_1$ state is decreasing in energy relative to both the $^1A_1$ state and $^3B_1$ state with basis set improvements. To estimate the size and direction of the remaining error we use the correspondence between the states in CH and CH_2. Previously we demonstrated a correspondence of the $^1A_1$ state of CH_2 with the $^2\Pi$ state of CH and the $^3B_1$ state with the $^4\Sigma^-$. If the $^1B_1$ state is bent to 90° then a hydrogen removed, the corresponding state in CH is determined to be the $^2\Sigma^-$ state.

Using this correspondence and the accurate work on CH by Lie et al.,[19] we can make an estimate of the remaining error as we did for the $^1A_1$-$^3B_1$ separation. The results of Lie et al. show the $^2\Sigma^-$ - $^2\Pi$ separation is too large by 0.02 eV, the $^2\Pi$ -$^4\Sigma^-$ separation is too large by 0.09 eV, and the $^2\Sigma^-$-$^4\Sigma^-$ separation is too large by 0.11 eV. In CH_2 these correspond to a $^1B_1$-$^1A_1$ separation too large by 0.02 eV, $^1A_1$-$^3B_1$ separation too large by 0.09 eV, and a $^1B_1$-$^3B_1$ separation too large by 0.11 eV. These corrections have been made to the CH_2 separations and are reported in Table I under `estimated`.

It might seem optimistic to think that a correction as small as 0.02 eV has any meaning, but we should note that HGII's computed $^1B_1-^1A_1$ 5-0 transition is too large by 0.03 eV.

Both our $^1A_1-^3B_1$ and $^1A_1-^1B_1$ separations are in agreement with HGII. Based on our results and trends observed, we believe the lower range of the HGII $^1A_1-^1B_1$ separation (1.08±0.05 eV) is correct. Our technique of determining the size and direction of the remaining error is helpful in adjusting the computed Franck-Condon factors to agree with experiment. The combination of this work and HGII yields a conclusive determination of the last observed transition as 5-0.

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Table I. Excitations energies for CH_2. Energies in eV.

BASIS SET

Transition	DZ	DZP	Large	Estimate[c]	HGI[d]	HGII[f]	SPBP[f]
				SCF			
$^1B_1-^3B_1$	1.86[a]	1.80	1.73				
$^1B_1-^1A_1$ [b]	0.87	1.24	1.25				
				CI			
$^1B_1-^3B_1$	1.94	1.69	1.56	1.45	1.56±0.02	1.47	1.61
$^1B_1-^1A_1$	0.97	1.15	1.09	1.07	1.08±0.1	1.08±0.05	1.10

a $^1B_1$ results from: S. V. ONeil, H. F. Schaefer, and C. F. Bender, J. Chem. Phys. 55, 162 (1971).

b two reference $^1A_1$ used, see ref.4.

c Estimated from trends described in text.

d reference 1

e reference 2

f reference 3

Table II. Total energies and optimum geometries for the three lowest

States of CH_2. QE is the quadruples estimate in eV.

Large basis (LRG) was run at the DZP optimum geometry. The

total energy is in hartrees and bond lengths in bohrs.

BASIS	<HCH	RCH	SCF energy	<HCH	RCH	CI energy	QE
$^1B_1$							
DZ[a]	150.5	2.017	-38.8452	143.8	2.063	-38.9114	
DZP	142.3	2.02	-38.8623	141.5	2.036	-38.9798	0.15
LRG			-38.8660			-39.0052	0.19
$^3B_1$							
DZ	130.5	2.03	-38.9137	133.7	2.07	-38.9825	0.08
DZP	129.4	2.03	-38.9282	132.4	2.045	-39.0416	0.15
LRG			-38.9333			-39.0622	0.18
$^1A_1$ 1ref							
DZ	106.1	2.09	-38.8620	105.1	2.14	-38.9447	0.14
DZP	102.4	2.11	-38.8863	102.4	2.11	-39.0183	0.24
LRG			-38.8935			-39.0411	0.29
$^1A_1$ 2ref							
DZ	104.6	2.09	-38.8770	105.2	2.14	-38.9472	
DZP	102.8	2.08	-38.9079	102.4	2.11	-39.0222	
LRG			-38.9157			-39.0453	

a $^1B_1$ DZ result from: S. V. ONeil, H. F. Schaefer, and C. F. Bender, J. Chem. Phys. 55, 162 (1971).